Carbohydrate Research, 44 (1975) 45–52
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FACILE PREPARATION OF DEOXY(THIOCYANATO)CELLULOSES

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(Received April 28th, 1975; accepted for publication, June 20th, 1975)

ABSTRACT

Deoxy(thiocyanato)celluloses were prepared by treating chlorodeoxycellulose fabrics with potassium thiocyanate in *N,N*-dimethylformamide. Under optimal reaction-conditions, more than 80% of the chlorine atoms in the cellulose derivative were replaced by thiocyanate groups. Both the chlorodeoxy- and deoxy(thiocyanato)-cellulose fabrics exhibited moderate antibacterial activities.

Variables studied were thiocyanate concentration, reaction time and temperature, and degree of substitution of the chlorodeoxycellulose in the fabrics being treated. The effect that each of these variables had on the replacement of chlorine atoms by thiocyanate groups was investigated. The tensile, wrinkle-recovery, and biocidal properties of the chlorodeoxy- and deoxy(thiocyanato)cellulose fabrics were also compared.

INTRODUCTION

The incorporation of the thiocyanate group as an integral part of the D-glucosyl residues of cellulose has been only cursorily investigated. Carson and MacLay[1] treated various *p*-toluenesulfonylated carbohydrates (including cellulose) with potassium thiocyanate in 2,4-pentanedione. Under these conditions, only half of the *p*-tolylsulfonyloxy groups were displaced by thiocyanate, and the reaction time required ranged from 7 to 11 h. However, we have found that over 80% of the chlorine atoms can be replaced by thiocyanate within 1 h by the reaction of chlorodeoxycellulose with potassium thiocyanate in *N,N*-dimethylformamide.

The present report describes the effect of the reaction conditions and the initial content of chlorine in the chlorodeoxycellulose on the chemical and physical properties of the resultant deoxy(thiocyanato)cellulose. Also, the antibacterial properties of both chloro- and thiocyanato-containing celluloses are reported.

EXPERIMENTAL

General. — The cellulose used was desized, scoured, and bleached cotton printcloth having 80 threads per inch in warp and filling. Phosphoryl chloride, *N*,*N*-dimethylformamide, sodium hydroxide, and potassium thiocyanate were reagent-grade, commercial materials.

Chlorodeoxycellulose was prepared by the phosphoryl chloride–*N*,*N*-dimethylformamide method[2], by using 14% phosphoryl chloride for 1 h at 63 or 78° to obtain different levels of chlorination. Chlorodeoxycellulose was converted into deoxy(thiocyanato)cellulose by reaction with various concentrations of potassium thiocyanate in *N*,*N*-dimethylformamide at the ratio of 40 g of the solution per g of chlorodeoxycellulose. The modified cellulose was washed with ice water for 10 min and tap water for 30 min, and air-dried.

Chlorine and sulfur were determined by a commercial laboratory; phosphorus was determined by X-ray fluorescence, and nitrogen by the Kjeldahl method at our laboratories. The degrees of substitution (d.s.) for chlorodeoxycellulose and deoxy(thiocyanato)cellulose were calculated from the chlorine and sulfur analyses, respectively. Infrared (i.r.) spectra for pellets of the cellulose derivatives in potassium bromide were recorded with a Perkin–Elmer Model 137B Infracord spectrophotometer*.

The breaking strength of the fabric in the warp direction was determined by ASTM method B-1682-64 (strip method). Wrinkle-recovery angles were measured by the Monsanto method (ASTM D-1295-67). Laundering durability of the modified cotton fabrics was determined by repeated washing and drying in an agitator type of washer (10-min hot-water wash) and tumble dryer (30 min of high-temperature drying); the commercial, AATCC (American Association of Textile Chemists and Colorists) standard detergent 124* was used. Antibacterial activity was determined by the parallel streak test (AATCC 100-1965) with *Staphylococcus aureus* and *Escherichia coli*.

RESULTS AND DISCUSSION

Effect of reaction time and temperature on conversion of chlorodeoxycellulose into deoxy(thiocyanato)cellulose. — The conversion of chlorodeoxycellulose (d.s. 0.35, 7.3% Cl) into deoxy(thiocyanato)cellulose was investigated at reaction times of 30–180 min and at reaction temperatures of 100–150° by using 20% potassium thiocyanate in *N*,*N*-dimethylformamide. Preliminary experiments indicated that anhydrous *N*,*N*-dimethylformamide was superior to aqueous *N*,*N*-dimethylformamide as the reaction solvent, and it was therefore used in all subsequent thiocyanation studies.

Thiocyanation was found to be time- and temperature-dependent; but very little, or none, of the chlorine was displaced below 125°. The d.s. of the resultant deoxy(thiocyanato)celluloses ranged from 0.06 to 0.29, depending on the reaction conditions. As shown in Table I, most of the ratios of sulfur to nitrogen in the deoxy(thiocyanato)celluloses were close to 1:1. Exceptions were the samples treated

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*Use of the name of a company or a product does not imply approval or recommendation of the product by the Department to the exclusion of products of other companies that may also be suitable.

for 180 min at 125° and for 75 min at 132°; however, the total d.s. of the chloro and thiocyanato groups in these materials agreed with those of other samples whose S/N ratios approached 1:1.

TABLE I

EFFECT OF REACTION TIME AND TEMPERATURE ON CONVERSION OF CHLORODEOXYCELLULOSE INTO DEOXY(THIOCYANATO)CELLULOSE

Reaction temp. (°C)	*Reaction time (min)*[a]	*Cl (%)*[b]	*S (%)*[b]	*N (%)*[b]	*Atomic ratio (S/N)*	*Final*	
						Cell-Cl[b] *(d.s.)*	*Cell-SCN*[b] *(d.s.)*
100	60	7.06	0.10	0.21	0.21	0.34	0
125		5.65	1.21	0.64	0.82	0.27	0.06
	180	3.37	3.56	1.15	1.35	0.16	0.19
132	75	3.33	3.84	1.27	1.32	0.16	0.20
140	60	3.22	3.94	1.65	1.04	0.15	0.21
	120	1.47	4.82	2.21	0.95	0.07	0.26
150	30	4.04	2.48	1.06	1.02	0.19	0.13
	60	1.37	5.19	2.23	1.02	0.06	0.28
	120	0.73	5.34	2.28	1.02	0.03	0.29

[a] Thiocyanations were conducted by reacting 20% potassium thiocyanate in *N*,*N*-dimethylformamide with chlorodeoxycellulose fabrics containing 7.3% of Cl (d.s. 0.35), using a bath ratio of 40 g of solution/g of Cell-Cl. After the solution cooled to 25°, the fabrics were washed with ice water (10 min) and tap water (30 min), and air-dried. [b] Uncorrected for % of P, moisture, and ash.

At 125°, the d.s. of the deoxy(thiocyanato)celluloses tripled (from 0.06 to 0.19) when the reaction time was tripled from 60 to 180 min. The d.s. (0.20) was comparable for a reaction time of 75 min at 132°. When the reaction time was doubled from 60 to 120 min at 140°, the d.s. increased from 0.21 to 0.26, representing 60 to 74% displacement of the chloro by the thiocyanato group.

Data for the experiments conducted show that 150° is probably the optimal temperature for conversion of chlorodeoxy- into deoxy(thiocyanato)-cellulose. This was particularly true for a reaction time of 60 min (d.s. 0.28), where 80% of the chloro groups were replaced.

There was no advantage in conducting the reaction for a longer time (e.g., 120 min) at 150°, as excessive yellowing occurred and there was only a slight increase in the overall d.s. (0.29). When other investigators[3] treated chlorodeoxycellulose under comparable conditions with potassium cyanide in *N*,*N*-dimethylformamide, the maximal displacement of the chloro group was only 65%. The greater nucleophilicity of thiocyanate relative to cyanide may explain this difference in reactivity.

The i.r. spectra of the products from treatment of chlorodeoxycellulose with potassium thiocyanate at different temperatures (see Fig. 1) afforded additional evidence that the reaction product was deoxy(thiocyanato)cellulose. A detailed spectroscopic study by Miller and White[4] showed that the thiocyanate linkage

(–S–C≡N) exhibits a narrow absorption band in the infrared at 4.7 μm, whereas the isothiocyanate linkage (–N=C=S) exhibits a broad absorption band at 4.6 to 5.0 μm. The absorption peak at 4.7 μm in Fig. 1 is characteristic of the thiocyanate group, and this peak increased in intensity as the d.s. of the deoxy(thiocyanato)cellulose increased.

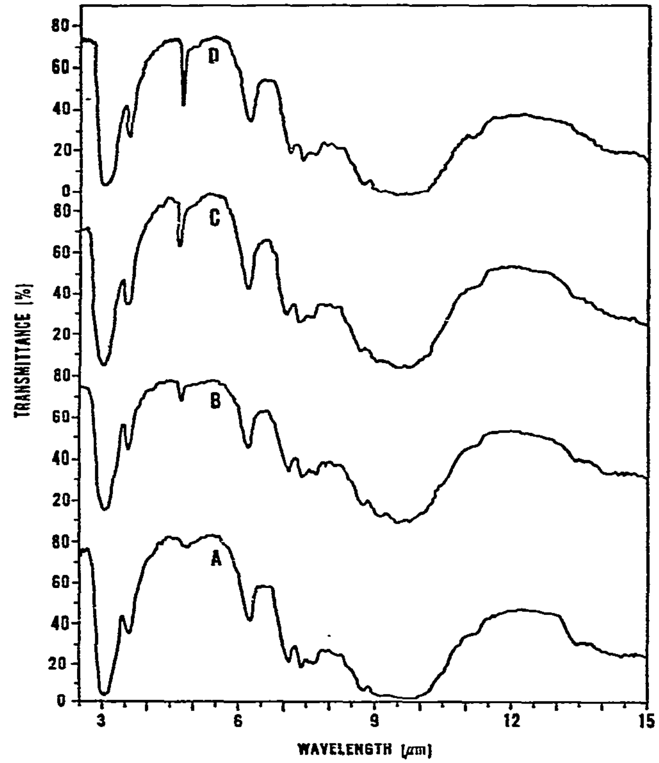

Fig. 1. I.r. spectrum of chlorodeoxycellulose printcloth (d.s. 0.35): (A) no treatment; treated with 20% KSCN in *N*,*N*-dimethylformamide for 1 h at (B) 125°, (C) 140°, and (D) 150°.

Effect of chlorine content on conversion of chlorodeoxycellulose into deoxy(thiocyanato)cellulose. — Chlorodeoxycelluloses of different d.s. (0.22 and 0.35) were treated with 20% potassium thiocyanate in *N*,*N*-dimethylformamide for various times and at various temperatures to determine whether the initial chlorine content affected the percentage of chlorine atoms replaceable by thiocyanate ion. The results are shown in Table II. Under comparable conditions of reaction, the percentage of chlorine replaced by thiocyanate was greater in lower d.s. than in higher d.s. chlorodeoxycelluloses; this difference was particularly evident for short reaction-times. In the reaction conducted for 60 min at 125°, conversion into deoxy(thiocyanato)cellulose was 41% with chlorodeoxycellulose of low d.s., and only 17% with high d.s. chlorodeoxycellulose. In the reaction performed for 30 min at 150°, thiocyanation for the chlorodeoxycellulose of low d.s. was 73% (d.s. 0.16) and 37% for the high d.s. material (d.s. 0.13).

TABLE II

EFFECT OF CHLORINE CONTENT ON CONVERSION OF CHLORODEOXYCELLULOSE INTO DEOXY(THIOCYANATO)CELLULOSE

Reaction temp. (°C)	*Reaction time (min)*[a]	*Cl (%)*[b]	*S (%)*[b]	*N (%)*[b]	*Atomic ratio (S/N)*	*Final*	
						Cell-Cl[b] *(d.s.)*	*Cell-SCN*[b] *(d.s.)*
125	60	3.02	1.66	0.60	1.21	0.14	0.09
140	120	0.59	3.46	1.55	0.97	0.03	0.18
150	30	1.36	3.06	1.26	1.06	0.06	0.16
	60	0.70	3.45	1.48	1.02	0.03	0.18
125	60	5.65	1.21	0.64	0.82	0.27	0.06
140	120	1.47	4.82	2.21	0.95	0.07	0.26
150	30	4.04	2.48	1.06	1.02	0.19	0.13
	60	1.37	5.19	2.23	1.02	0.06	0.28

[a] Experimental conditions as listed in Table I, footnote a, with the exception that the first four samples listed were chlorodeoxycellulose containing 4.75% of Cl (d.s. 0.22), whereas the last four samples had a chlorine content of 7.3% (d.s. 0.35). [b] Uncorrected for % of P, moisture, and ash.

However, under more-favorable reaction conditions (longer reaction-time, or higher temperature, or both), the percentage of chlorine atoms replaced by thiocyanate groups was independent of the original chlorine content of the cellulose. For example, displacements of chlorine were 82 and 74%, respectively, for the low and high d.s. chlorodeoxycelluloses when the reaction was conducted for 120 min at 140°. Results were similar for 60 min at 150° (82 and 80% conversion), regardless of the original d.s. of the chlorodeoxycellulose. The more highly chlorinated celluloses were used in subsequent experiments, because higher degrees of substitution were needed in order to impart any biocidal activity to the modified-cellulosic fabrics.

Effect of thiocyanate concentration on conversion of chlorodeoxycellulose into deoxy(thiocyanato)cellulose. — As shown in Table I, the preferred times and temperatures for optimal thiocyanation were 120 min at 140°, and 60 min at 150°. Therefore, various concentrations of potassium thiocyanate in *N*,*N*-dimethylformamide were allowed to react with chlorodeoxycellulose of d.s. 0.35 under these two sets of conditions. The results in Table III show a progressive displacement of chlorine as the concentration of the thiocyanate was increased; this is also shown in Fig. 2.

There is only a slight advantage in conducting the reaction for 60 min at 150° instead of for 120 min at 140°. Conversion was ~17–23% with 2% thiocyanate and ~34–37% with 5% thiocyanate. With 10% thiocyanate, displacement of the chloro group increased to 57%. Optimal displacement was obtained with 20% thiocyanate, 74–80% of the chloro groups being replaced to give a deoxy(thiocyanato)cellulose of d.s. 0.26–0.28.

TABLE III

EFFECT OF THIOCYANATE CONCENTRATION ON CONVERSION OF CHLORODEOXYCELLULOSE INTO DEOXY(THIOCYANATO)CELLULOSE

Reaction temp. (°C)	*Reaction time (min)*[a]	*% KSCN in $HCONMe_2$*	*Cl (%)*[b]	*S (%)*[b]	*N (%)*[b]	*Atomic ratio (S/N)*	*Final*	
							Cell-Cl[b] *(d.s.)*	*Cell-SCN*[b] *(d.s.)*
140	120	2	6.09	1.21	0.63	0.84	0.29	0.06
		5	4.84	2.25	1.04	0.94	0.23	0.12
		10	3.67	3.68	1.57	1.02	0.17	0.20
		20	1.47	4.82	2.21	0.95	0.07	0.26
150	60	2	5.19	1.56	0.74	0.92	0.24	0.08
		5	4.04	2.47	1.15	0.94	0.19	0.13
		10	3.05	3.70	1.63	0.99	0.14	0.20
		20	1.37	5.19	2.23	1.02	0.06	0.28

[a] Experimental conditions listed in Table I, footnote a. [b] Uncorrected for % of P, moisture, and ash.

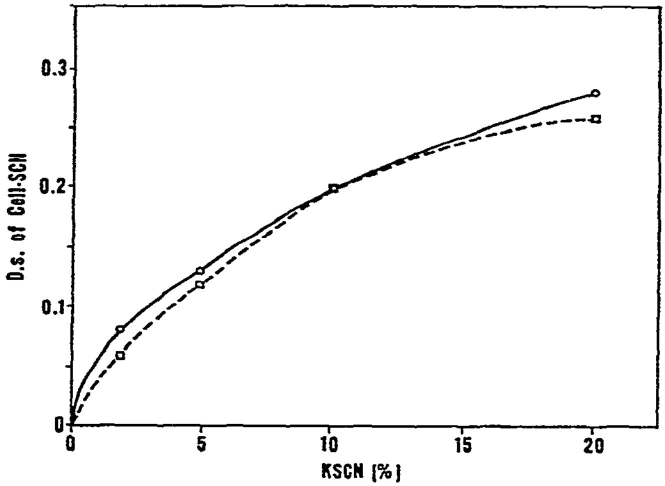

Fig. 2. Plot of d.s. of deoxy(thiocyanato)cellulose *versus* % of KSCN in *N,N*-dimethylformamide (— — — —, 2 h at 140°; ————, 1 h at 150°).

Textile properties of chlorodeoxycellulose and deoxy(thiocyanato)cellulose fabrics. — Tensile and recovery properties [breaking strength (b.s.) and wrinkle-recovery angle] varied moderately between chlorodeoxycellulose and deoxy(thiocyanato)cellulose fabrics. The breaking strength of the chlorodeoxycellulose fabric (d.s. 0.35, 7.3% Cl) was about two-thirds of that of the untreated control. Further conversion into a fabric containing equal proportions of chloro and thiocyanate groups only slightly lowered the tensile strength (58% overall retention) as shown in Table IV. Laundering of the chlorodeoxy- and deoxy(thiocyanato)cellulose fabrics moderately lessened the strength (51 and 47% overall b.s. retention, respectively). Wrinkle-recovery angles (warp+fill) were comparable for the chlorodeoxycellulose and the deoxy(thiocyanato)cellulose fabrics; conditioned values ranged from 130 to 140°, and wet recovery ranged from 210 to 240°.

TABLE IV

TEXTILE PROPERTIES OF CHLORODEOXYCELLULOSE AND DEOXY(THIOCYANATO)CELLULOSE FABRICS

Cell-Cl[a] *(d.s.)*	*Cell-SCN*[a] *(d.s.)*	*B.s.*[b] *(lb)*	*Strength retained (%)*[c]	*Launderings*	*Parallel-streak test*[d]	
					Reading	*Rating*
0.35	0	30.0	63	0	NUG	P
0.35	0	24.5	51	10	VSUG	P
0.16	0.20	27.9	58	0	VSUG	P
0.19	0.13	22.2	47	10	NUG	P
—[e]	—	47.7	(100)	0	UG	F

[a]Derived from data in Table I. [b]B.s. = breaking strength. [c]Based on untreated printcloth. [d]F = failed; NUG = no undergrowth; P = passed; UG = undergrowth; VSUG = very slight undergrowth. [e]Untreated printcloth.

The antibacterial properties of the chloro- and thiocyanato-containing cotton fabrics, before and after laundering, were tested. The parallel-streak test showed that, even before being laundered, the low d.s. chlorodeoxycellulose fabrics (d.s. 0.22, 4.75% Cl), and the deoxy(thiocyanato)cellulose fabrics derived therefrom, were not noticeably germicidal. Preliminary results, however, indicated that deoxy(thiocyanato)cellulose fabrics derived from high-d.s. chlorinated material had moderate biocidal activity. This activity was enhanced by laundering (see Table IV); the streak-test readings improved from "very slight undergrowth" to "no observable growth" after 10 launderings. This slight improvement in biocidal effectiveness may be consistent with a lowering of the d.s. of the deoxy(thiocyanato)cellulose after laundering; the slow release of thiocyanic acid (HSCN) by hydrolysis of the thiocyanate group would thereby increase the germicidal protection. Conversely, the chlorine-containing fabric of high d.s. lost some of its initial, biocidal activity after ten launderings. Both modified fabrics, however, offered some germicidal protection relative to untreated cotton fabrics (which exhibited undergrowth and failed the streak test).

ACKNOWLEDGMENTS

The authors thank Biagio Piccolo for the X-ray fluorescence determinations, John Mason for the Kjeldahl analyses, Mildred Williams for evaluating the tensile and recovery properties of the fabrics, and Leontine Daniels for recording the infrared spectra of the modified celluloses.

REFERENCES

1 J. F. Carson and W. D. Maclay, *J. Am. Chem. Soc.*, 70 (1948) 2220–2223.
2 T. L. Vigo and C. M. Welch, *Carbohydr. Res.*, 32 (1974) 331–338.
3 A. I. Polyakov and Z. A. Rogovin, *Vysokomol. Soedin.*, 5 (1963) 11–17; *Chem. Abstr.*, 59 (1963) 6,604h.
4 F. A. Miller and W. B. White, *Z. Elektrochem.*, 64 (1960) 701–707.